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Region-specific emission factors for Brazil increase the estimate of nitrous oxide emissions from nitrogen fertiliser application by 21%

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Abstract

The use of synthetic nitrogen fertilisers is one of the most important land management practices proposed to improve crop and pasture productivity. The use of such fertilisers in excess can lead to greenhouse gas (GHG) emissions, linked to climate change, as well as ammonia (NH_3) emissions, linked to eutrophication and soil acidification.. This context is especially important in Brazil, which is responsible for a significant share of the food produced in the world. To assess the impact of the use of nitrogen fertilisers, we conducted a structured review of Brazilian studies on the emission of nitrous oxide (N_2O ; 11 studies) and ammonia volatilisation (NH_3 ; 13 studies) from nitrogen fertiliser application. The current emission factors (EF) suggested by the IPCC for N_2O and NH_3 (1 and 11%, respectively) are lower than the mean values we found in our review (1.12 and 19%, respectively). Our results showed that non-urea fertilisers (ammonium nitrate or ammonium sulphate) had a lower emission factor (EF) for N_2O (1.07 and 0.60%, respectively) and NH_3 (3.17 and 14%, respectively) in comparison with urea. The use of nitrification and urease inhibitors resulted in a reduction of the EFs of N_2O (74% lower) and NH_3 (43% lower) when compared with the Urea EF. Urea is the most common fertiliser used in Brazil, and the change for non-urea fertilisers or the use of inhibitors could lead to a reduction of 23% in the total N_2O inventory. The use of the new region-specific EFs results in an increase of 21% in the final N_2O emission inventory.

Keywords: nitrous oxide, emission factor, Brazil, ammonia, synthetic fertiliser

1. Introduction

The global demand for food due to human population growth and changing diets is putting pressure on the efficiency and sustainability of food production systems (Conijn et al., 2018). The increased use of land, pesticides and nutrients has played an important role in increasing agricultural production and delivering food security for many nations during the Green revolution, but these gains have been accompanied by negative impacts on the environment, especially greenhouse gas (GHG) (Davis et al., 2016) and ammonia (NH₃) emissions (Steffen et al., 2015), as well as nitrate leaching (Wang et al., 2019). The current challenge faced by the agricultural sector is to further increase production, while at the same time reducing or mitigating the environmental impacts. The pressure for food production will increase even further in the next decade (Calicioglu et al., 2019), and the potential for increasing productivity relies on relatively few areas. Currently, Brazil is responsible for 14% of beef, 12% of poultry, 41% of sugarcane and 30% of coffee exports (FAOStat, 2018). The Brazilian food system needs to be re-engineered to address future demand, and sustainable intensification is one promising strategy for the region.

“Sustainable intensification” is linked to the concept of agricultural efficiency (producing more per unit of input or maintaining production with less input - FAO, 2004), merged with the concept of sustainability, that considers the impact of practices on environmental, social and economic sectors (Garnett et al., 2013; Pretty, 2018). Among the concerns on the environment are GHG emissions (causing climate change and putting extra-pressure on food production in Brazil). In the context of sustainable intensification, the optimal use of synthetic N fertilisers, and effective recycling of livestock manures, on crops and grassland will be important (Bouwman et al., 2013). Ammonia emissions are associated with environmental impacts such as eutrophication and soil acidification (Fowler et al., 2013), as

well as effects on human health associated with the formation of fine particulates (Stokstad et al., 2014). Ammonia emissions also represent an indirect form of N₂O loss (IPCC, 2006).

In order to assess the sustainability of food production in Brazil, it is imperative that the data employed to estimate these environmental impacts are as accurate as possible, to reliably underpin mitigation policies and management strategies. Improved estimations using robust key emission factors would support more accurate inventories and carbon footprints and help to target effective mitigation practices. Currently, N₂O emission and NH₃ volatilisation in Brazil are estimated by the IPCC Tier 1 method (using a single default emission factor expressed as a fraction of the N applied to the soil), based on Bouwman (1996). The limitations of such an approach are that the same emission factor (EF) is used irrespective of the fertiliser type, soil type, land use (arable or grass), and different climates throughout Brazil. The synthesis of appropriate data would provide a much-needed improvement over the current IPCC Tier 1 approach, leading to an inventory that reflects the region's fertiliser management practices, soils and climate. This paper focusses on direct N₂O and NH₃ fluxes and emission factors derived from synthetic fertiliser inputs to agricultural systems. The main goal of this paper is to review the available literature and define region-specific emission factors applicable to the Brazilian conditions to better understand the sensitivity of the choice of EFs used in the Brazilian GHG inventory.

2. Materials and methods

We performed a systematic literature review focusing on direct N₂O emission and NH₃ volatilisation in Brazil. The literature search was performed using “Web of Science”, “Science Direct”, “Scielo” and “Google Scholar” search engines. The search was carried out using all combinations of the following keywords (and their translations in Portuguese): “nitrous oxide”, “ammonia”, and “fertiliser”. The resulting reference lists of publications were screened and

retained if they met the following criteria: (1) published in peer-reviewed journals; (2) performed in Brazil; (3) not conducted in greenhouses or manipulated weather conditions. After discarding publications that did not meet the criteria, the final database for analysis included 11 papers for N₂O (n = 63 experiments) and 13 papers for NH₃ (n = 83 experiments) (databases available in the Supporting Information).

For each retained publication, a specific study code was assigned and the following characteristics were recorded in the database: authors, year, region, latitude, longitude, elevation (m.a.s.l.), Koppen-Geiger climatic classification, annual rainfall (mm), average annual temperature (°C), soil type, crop or pasture genus, number of treatments, number of replications, season, N fertiliser type, application method and rate, cumulative N₂O emissions (kg N₂O-N ha⁻¹), cumulative NH₃ volatilisation (kg NH₃-N ha⁻¹) and emission factors (EF). The most common missing data in reviewed papers were related to climate characteristics. These gaps were filled where necessary using data from the nearest weather station (based on the location information provided in the paper). When the EF was not reported in the study, we derived it according to Eq 1. We used the software WebPlotDigitizer to extract precise numbers when data were presented only as figures.

$$EF(\%) = \left(\frac{Emission_{FT} - Emission_C}{Applied\ fert} \right) * 100 \quad (1)$$

Where:

EF (%) = Emission Factor, in %;

Emission_{FT} = Emission or volatilisation from fertiliser treatment (in kg N ha⁻¹ year⁻¹);

Emission_C = Emission or volatilisation from control treatment (in kg N ha⁻¹ year⁻¹);

Applied fert: Amount of fertiliser applied (in kg N ha⁻¹ year⁻¹).

Due to the lack of statistical information reported in some studies (standard deviation, coefficient of variation, p -value, etc.), we were not able to perform a formal meta-analysis. Descriptive statistics were calculated for each variable (mean, minimum, maximum, range, standard deviation and coefficient of variation). To account for the precision of each study, the number of samples described in each paper was used as a weighting factor (studies with more replicates were assigned greater importance). One-way and two-way ANOVA were then used to investigate the structural relationship between the responses, testing the N₂O emissions against the soil type, soil texture and land use. All statistical differences were checked to $p < 0.05$, but we were not able to find statistical differences. Pearson's correlation coefficient was calculated. All statistical analyses were performed using R (R Core Studio, 2018).

We consulted the FAO databases (FAOStat, 2018) to estimate the total annual quantity of N fertiliser used in Brazil. Based on the data available, we derived estimates for total N₂O emission, NH₃ volatilisation and NO₃⁻ leaching (summing the direct N₂O emission with the indirect emission from NH₃ volatilisation and NO₃⁻ leaching – Supplementary) using the IPCC Tier 1 EFs and the new region-specific EFs derived from this review for direct N₂O and NH₃. (Table 1).

3. Results

3.1 Literature evaluation

Most of the papers are from the Central-South region of the country (latitudes 23° to 10° S), in a transition from tropical to subtropical climates. For the N₂O database, 20% of the papers did not report the EF, carbon content or bulk density of the soil, only 10% reported the soil ammonium (NH₄⁺) and nitrate (NO₃⁻) content and 30% reported crop yield. Other factors were reported more frequently, including soil texture and classification (90% of the papers), soil pH and duration of the experiment (100% of the papers). A similar scenario was found for

the NH₃ database, where soil texture (70%), soil classification (90%), soil pH and experiment duration (100%) were often reported, while crop yield and bulk density were reported in only 10% of the papers. Soil NH₄⁺ or NO₃⁻ content were not reported in any paper. The average duration of the experiments was 188 and 55 days for N₂O and NH₃, respectively, and the average fertiliser application rate was 127 and 92 kg N ha⁻¹ for N₂O and NH₃, respectively.

3.2 N₂O emission and EF

The N₂O emission was positively correlated with the fertiliser application rate ($\rho=0.55$), soil texture (sand content, $\rho=0.27$) and pH ($\rho=0.25$), and the N₂O EF was negatively correlated with the soil bulk density ($\rho= -0.60$). The EF ranged from 0.01% to 6.70%, and 75% of the EFs reported (or calculated) were in the range given by the IPCC for the Tier 1 default EF (0.30% to 3%, mean 1% - IPCC, 2019). Overall, the average N₂O-EF was 1.12% (95% confidence Interval = 0.75 to 1.48%; median = 0.78%). Fertiliser type influenced the final EF, with a higher value found when using urea (1.45%), and a lower when using ammonium sulphate (0.60%) (Figure 1). Lower EFs were found when using nitrification inhibitors (NI) and coated urea (CU), reducing the average urea EF by 74% and 61%, respectively, with results lower than the average IPCC EF (Figure 1). The mean EF for the Oxisols was lower than the IPCC Tier 1 default, independent of the fertiliser type, while for other soil types (Ultisol and Non-Classified) the EFs were higher than the IPCC Tier 1 default (Figure 2), although there were very few data for Ultisols. The effect of the NI was greater on the Oxisol (86%) (Figure 2). Soil texture influenced the final EF, with lower values found on loam and sandy clay loam soils than on sandy loam soils (Figure 3). Land use also influenced EF, with results lower than the IPCC average for pastures (*Brachiaria* and *Pennisetum*) and higher higher than the IPCC average for crops (*Saccharum* and *Zea*) (Figure 4).

3.3 NH_3 volatilisation and EF

Cumulative NH_3 volatilisation was negatively correlated with soil pH and rainfall ($\rho = -0.23$ and -0.40 , respectively) and positively correlated with the fertiliser application rate ($\rho = 0.39$), while the NH_3 EF was negatively correlated with temperature ($\rho = -0.30$). The EFs ranged from 0 to 59%. Overall, the average NH_3 -EF was 19% (median = 18%), higher than the IPCC default Tier 1 $\text{Frac}_{\text{GASF}}$ value of 11% (IPCC, 2019). Fertiliser type influenced the final EF, with a higher value found when using urea (1.45%), and a lower value when using non-urea, i.e., ammonium sulphate (0.60%) and ammonium nitrate (1.07%) (Figure 1). Lower EFs were found when using urease inhibitors (UI) and coated urea (CU), reducing the average urea EF by 43 and 34%, respectively, when compared with the Urea EF (Figure 1). Soil type and land use had no influence on the final EF (Figure 2 and 4), but we found soil texture resulted in significant differences ($p < 0.05$), with lower EFs for loam and sandy clay loam soils than on sandy loam soils (Figure 3).

3.4 N fertiliser emission budget

The most common fertiliser used in Brazil is urea (52%), followed by ammonium nitrate (11%) and ammonium sulphate (10%), accounting for 73% of the total N-fertiliser used in the country (FAOstats 2018, Table 1 – Supplementary Information). The remainder of the N fertiliser (27%) is compound fertiliser, i.e. N in combination with phosphorus (P) and potassium (K) (e.g. potassium nitrate, sodium nitrate, NPK, etc). When applying the mean EFs derived from this study by fertiliser type for Brazil, the total N_2O -N emission budget increased by 21% compared with the IPCC Tier 1 EF (Figure 5 and Supplementary Information Table 1). This was mostly associated with revisions to the N_2O and NH_3 EFs for urea, with increases in the emission estimates of 45% and 73%, respectively, compared with using the IPCC Tier 1 default EF. If all the urea applied in Brazil were to be treated with a nitrification and urease

inhibitor (Figure 5), the N₂O-N emission for urea use would decrease by 43%, resulting in a final emission budget 23% lower than the current estimate using the IPCC Tier 1 default EFs (Figure 5).

4. Discussion

As recommended by Buckingham et al. (2014) and Gilsanz et al. (2016), we strongly advise researchers to follow standard protocols describing the data and adhere to a minimum reporting requirement so that the data can be used by future meta-analyses (Buckingham et al., 2014). More conclusions could have been drawn from this review if the authors of previous studies had systematically reported important data, such as soil NO₃⁻ and NH₄⁺ content, bulk density, soil carbon and crop yield. Furthermore, only three studies analysed both N₂O emission and NH₃ volatilisation (da Silva Paredes et al., 2014; Martins et al., 2015 and Martins et al., 2017). More research that focusses on nitrogen use efficiency and multiple pathways of N loss is necessary to provide a more complete understanding of the fate of N inputs in tropical systems. The conclusions drawn from this review are limited by the number of studies available in Brazil.

The range of EFs reported or derived from the literature reflect the variability in emissions across different N sources, different soil types and different land uses, leading to high uncertainty (Figures 1 to 4). The average EF for direct N₂O emission (across all fertiliser types, application rates, soils) in this study was 1.12%, similar to the new 2019 IPCC Tier 1 default. A recent study in the UK showed similar results for fertiliser applications to grassland (EF = 1.12% - Cardenas et al., 2019), while a study in New Zealand reported lower values (0.60% - van der Weerden et al., 2016). The average emission factor for NH₃ volatilisation was 19%, which is 72% higher than the IPCC default value (11%), but similar to the global average

of 18% found by Pan et al (2016). Non-urea fertilisers (ammonium nitrate and ammonium sulphate) had lower EFs for both N_2O and NH_3 (Figure 1). In contrast, Harty et al. (2016) reported that changing the N fertiliser source from calcium ammonium nitrate to urea leads to a reduction from 58 to 87% in the direct N_2O -EF. From our study, we show that the non-urea fertilisers have, on average, a 61% lower N_2O -EF than urea fertilisers (Figure 1).

Tropical conditions (humid and warm soil) favour rapid urea hydrolysis, increasing the rate of NH_3 volatilisation (Sommer et al., 2004). The soil pH observed was generally low, ranging from 4.20 to 6.20 (especially in Oxisols, average pH 4.5). In such conditions, nitrification is inhibited, limiting NO_3^- formation and N_2O emissions (Mørkved et al., 2007) (Figure 2). In our study, even in soils with low pH, urea showed the higher N_2O EF (Figure 2). Urea application generates localised zones of higher pH, which drives NH_3 volatilisation but also favours nitrification and NO_3^- formation and consequently, N_2O emissions (Wang et al., 2018). Clay content has been identified as one of the main edaphic factors controlling the N_2O EF (Wang et al., 2018), with EFs decreasing exponentially with increasing soil clay content due to a reduction in gas diffusivity, promoting N_2O reduction to N_2 through denitrification (Gu et al., 2013). This may explain the lower N_2O EF for clay and loam soils (Figure 3) and Oxisols (which have a higher clay content than Ultisols, Figure 2) in this review. The low N_2O EF found on tropical pastures (Figure 4) may be related to biological nitrification inhibition (BNI), a well-known process common in *Brachiaria* pastures (Subbarao et al., 2009). Compounds exuded from the roots of some *Brachiaria* species inhibit the nitrification process, consequently reducing the emission of N_2O and leaching of NO_3^- . (Arango et al., 2014).

Our review showed that the use of nitrification and urease inhibitors resulted in lower EFs for N_2O and NH_3 (74% and 43%, respectively, Figure 1), leading to a lower N_2O emission budget when compared with the budget calculated using the 2019 IPCC EFs (Figure 5). This

235 agrees with reports from studies in temperate climates (Cameron et al., 2014; Abalos et al.,
 236 2014 Misselbrook et al., 2014; Li et al., 2017). Ammonia volatilisation was also reduced with
 237 the use of urease inhibitors, similar to what has been found in temperate climates (Pan et al.,
 238 2016). The use of nitrification inhibitors results in a lower nitrification rate, allowing more time
 239 for the plants to absorb the applied NH_4^+ , but at the same time can stimulate more NH_3
 240 volatilisation (Soares et al., 2012, Abalos et al., 2014). Other factors, such as runoff and soil
 241 moisture content (due to more rainfall) and a quicker metabolism of the soil biomass (due to
 242 higher temperature in the tropics) also affects the N dynamics in tropical soils (Akiyama et al.,
 243 2000). The use of inhibitors can potentially improve the N use efficiency of fertilisers, leading
 244 to lower agronomic losses. Other studies have shown that the use of inhibitors can reduce NO_3^-
 245 leaching losses (Monaghan et al., 2013), increase plant assimilation of NH_4^+ (Akiyama et al.,
 246 2013), and increase crop/pasture yield (depending on the combination of inhibitor and cropping
 247 systems) (Abalos et al., 2014; Li et al., 2017). Urea is the most common fertiliser in Brazil due
 248 to its N content (46%), having a high density of N at a low cost. The use of non-urea fertilisers
 249 could lead to lower total GHG emissions (Figure 5). An important factor to consider is the
 250 impact on farmer costs due to the higher price of more efficient fertilisers and inhibitors in
 251 comparison with urea (Rose et al., 2018). The adoption of such technologies voluntarily will
 252 depend on products affordability for farmers, which may, in turn, depend on subsidy
 253 interventions (Tzemi and Breen, 2019). According to Carswell et al. (2018), there is no
 254 economic incentive for the farmer to use lower environmental impact option unless externality
 255 costs are incorporated into fertiliser prices. Another possible mitigation option is the sub-
 256 surface application/incorporation of urea-based N fertiliser, which can reduce the NH_3
 257 volatilisation by 63% (Huang et al., 2016). In our study, all the experiments reviewed applied
 258 the fertiliser to the soil surface (most manually). Management techniques such as splitting the

fertiliser application can potentially reduce N₂O emission (Bell et al., 2015; Cardenas et al., 2019; Borges et al., 2019) and NH₃ volatilisation (Huang et al., 2016).

The N₂O budget calculated for Brazil in this paper represents the best estimate of the N₂O emission using the currently available data, including uncertainties, especially regarding NO₃⁻ leaching factors (not reviewed in this study) that precede indirect N₂O emissions. In our review, all the experiments evaluating NH₃ volatilisation used chamber-methods. As pointed out by Jiang et al. (2017), chamber methods can over-or-underestimate the final emissions, depending on the difference in temperature, humidity and airflow within and outside the chamber. To develop EFs for use in emission inventories or farm/regional scale budgets, appropriate micrometeorological methods should be used which do not influence the emission (e.g. Denmead et al., 1993; Flesch et al., 2005; Misselbrook et al., 2005). Chamber studies can give useful comparative information on influencing factors and the efficacy of potential mitigation methods (Chambers and Dampney, 2009), which may be used to inform empirical or process-based models to derive EF though such models should be evaluated against micrometeorological datasets. Further studies in a wider range of Brazil are necessary to properly evaluate EFs across highly variable climate and soils in the country. Revised NH₃ emission factors could also inform more accurate environmental footprints for food products in Brazil, especially livestock products, in other environmental impact categories, such as eutrophication and acidification (Leip et al., 2015).

5. Conclusion

Our results showed that non-urea fertilisers had a lower EF for N₂O and NH₃ in comparison with urea. When nitrification or urease inhibitors were used, the final N₂O-EF and NH₃-EF from urea was significantly reduced. Based on our estimation, the complete budget of N₂O emission (direct and indirect) using the IPCC Tier 1 approach is 61,442 Mg

N₂O (for the year 2016). Use of the region-specific direct N₂O and NH₃ EFs increases this N₂O emission budget to 74,638 for the same year. This region-specific estimation would be reduced by 23% if all urea used in Brazil were incorporated with nitrification and urease inhibitors. Management practices such as the sub-surface application of N fertiliser could further reduce the impact of the fertiliser applications. When possible, specific policies should aim to reduce the price of, and/or provide subsidies for non-urea fertilisers or inhibitor-treated urea, given that at the current market prices most farmers would prefer to purchase urea.

We recognise that our results are limited by the number and geographic locations of the published studies that met our selection criteria for inclusion in the analysis. Further research on agricultural N loss pathways in Brazil should be prioritised since this is an important country for global food production. Given the current trends in food demand and the pressure for reducing deforestation, sustainable intensification on current grassland and cropland in Brazil will be necessary, where best management practices for fertiliser use are adopted to improve N use efficiency and minimize N losses.

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309

310 **Contributions**

311 A.M.M. built both databases, J.G. and A.M.M. performed the statistical analysis and
312 calculated the Emission factors and the Brazilian N₂O budget; A.M.M. wrote the manuscript
313 in close collaboration with D.C., C.A., J.G. and D.S. All the authors discussed the results and
314 provided input to the manuscript.

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Figures Subtitles

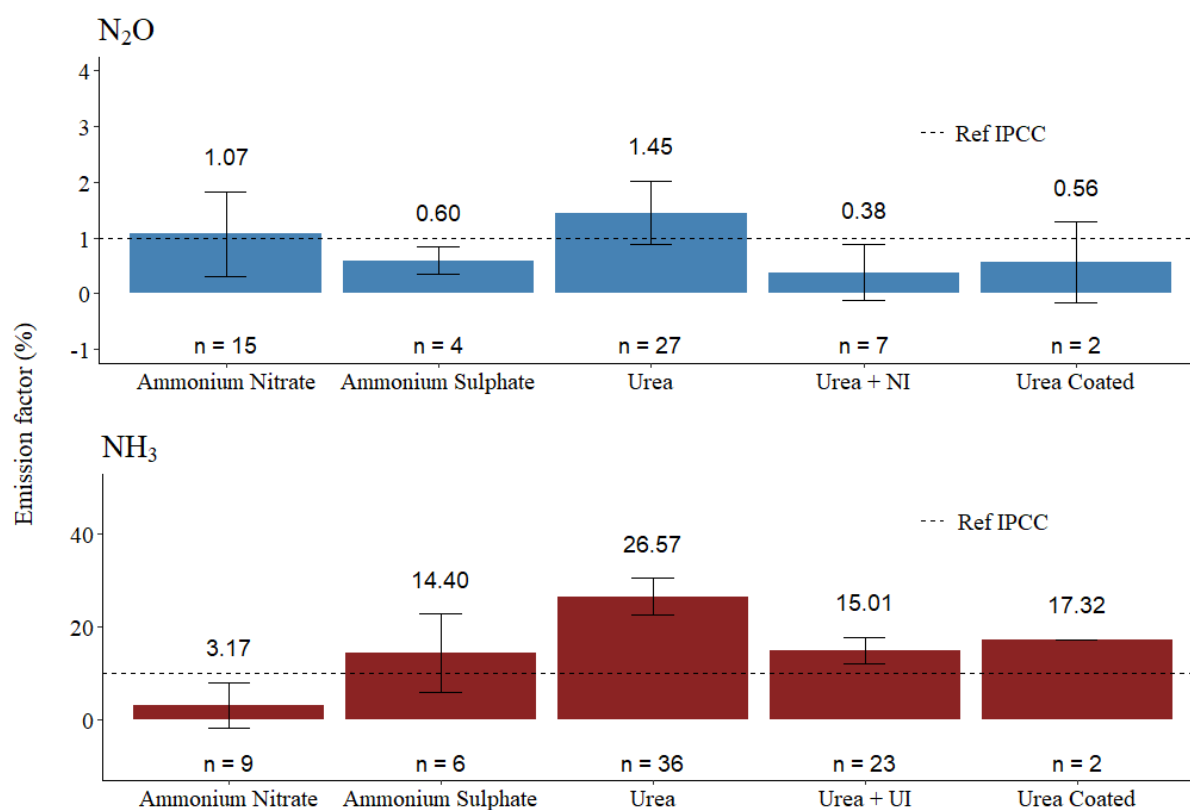


Figure 1. Emission factors for nitrous oxide and ammonia emissions, by fertiliser type. The dashed horizontal line marks the IPCC Tier 1 Default value for N₂O (1%) and NH₃ (11%). The error bars represent the 95% confidence interval. Urea+NI: urea applied with nitrification inhibitor; Urea+UI: urea applied with urease inhibitor. The “n” represents the number of experiments.

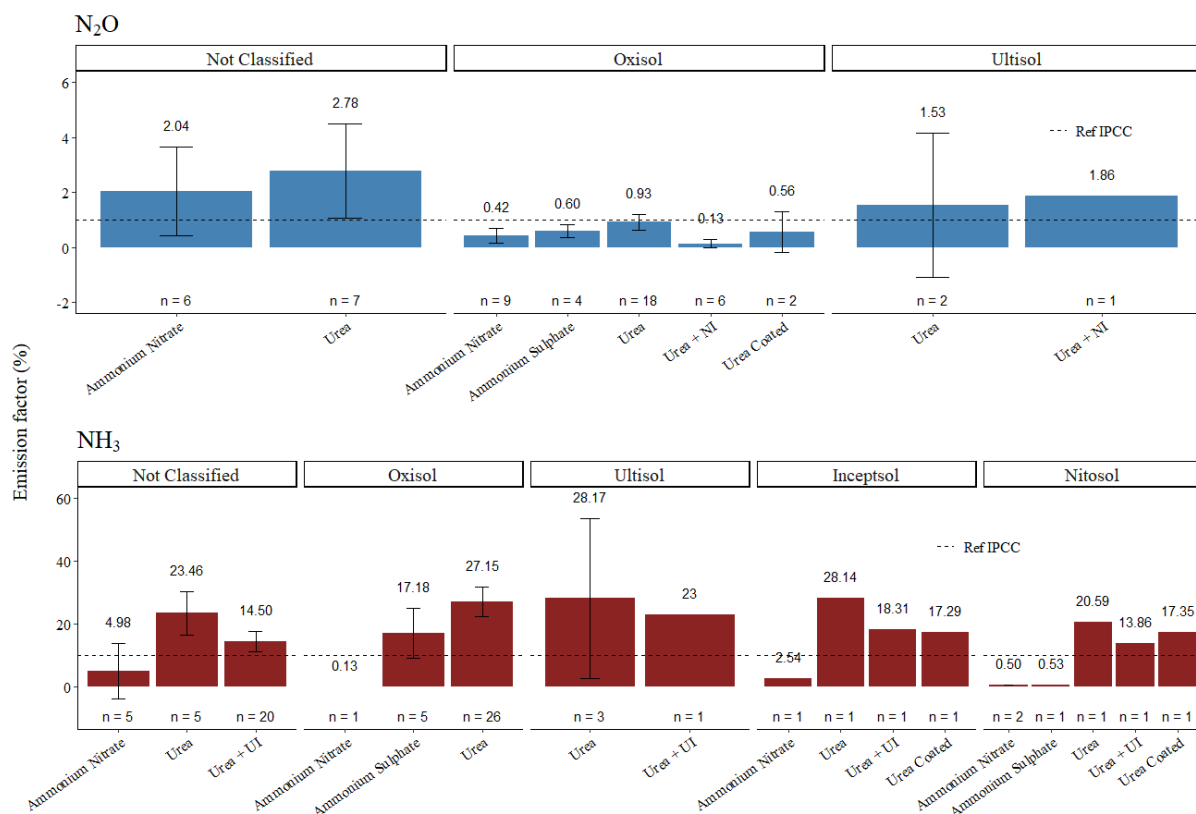


Figure 2. Emission factors for nitrous oxide and ammonia, by fertiliser and soil order. The error bars represent the 95% confidence interval. The horizontal dashed line marks the IPCC default value for N₂O (1%) and NH₃ (11%). Urea+NI: urea applied with nitrification inhibitor; Urea+UI: urea applied with urease inhibitor. The “n” represents the number of experiments.

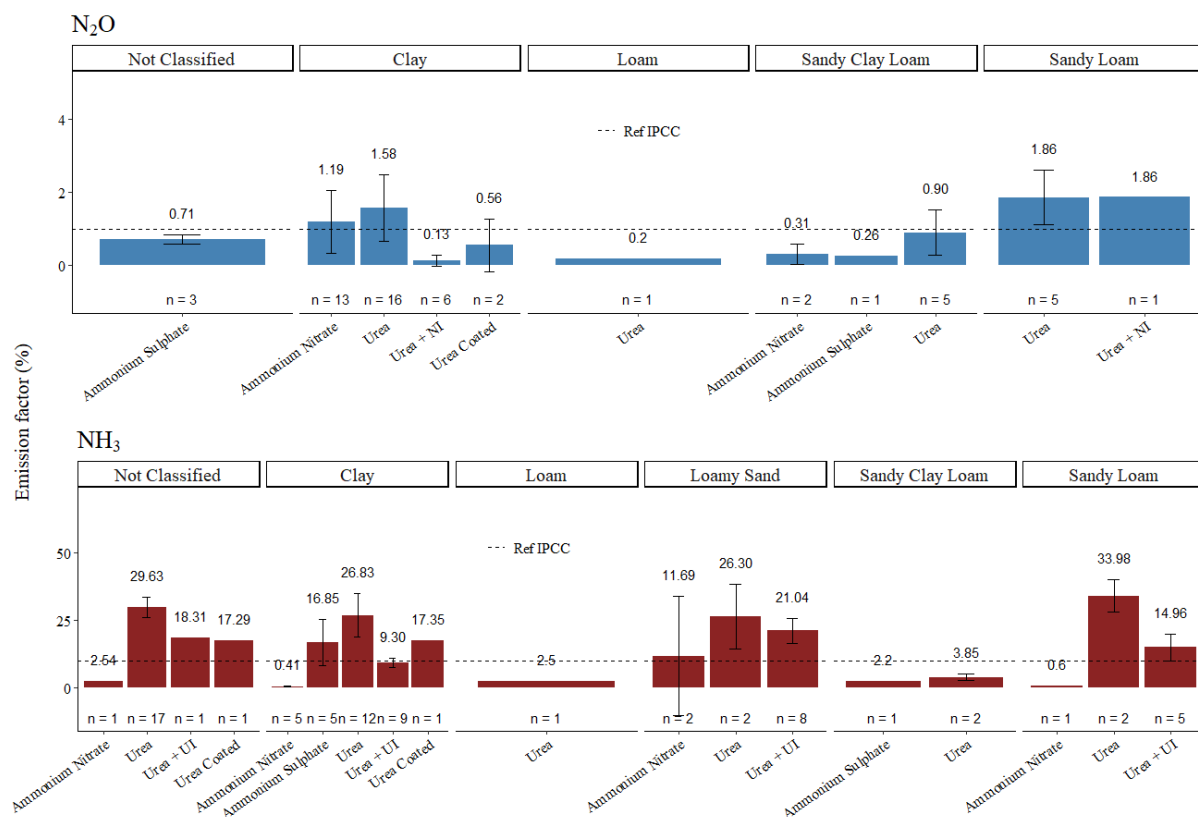


Figure 3. Emission factors for nitrous oxide and ammonia, by fertiliser type and soil texture. The bars represent the 95% confidence interval. The dashed horizontal line marks the IPCC default value for N₂O (1%) and NH₃ (11%). Urea+NI: urea applied with nitrification inhibitor; Urea+UI: urea applied with urease inhibitor. The “n” represents the number of experiments.

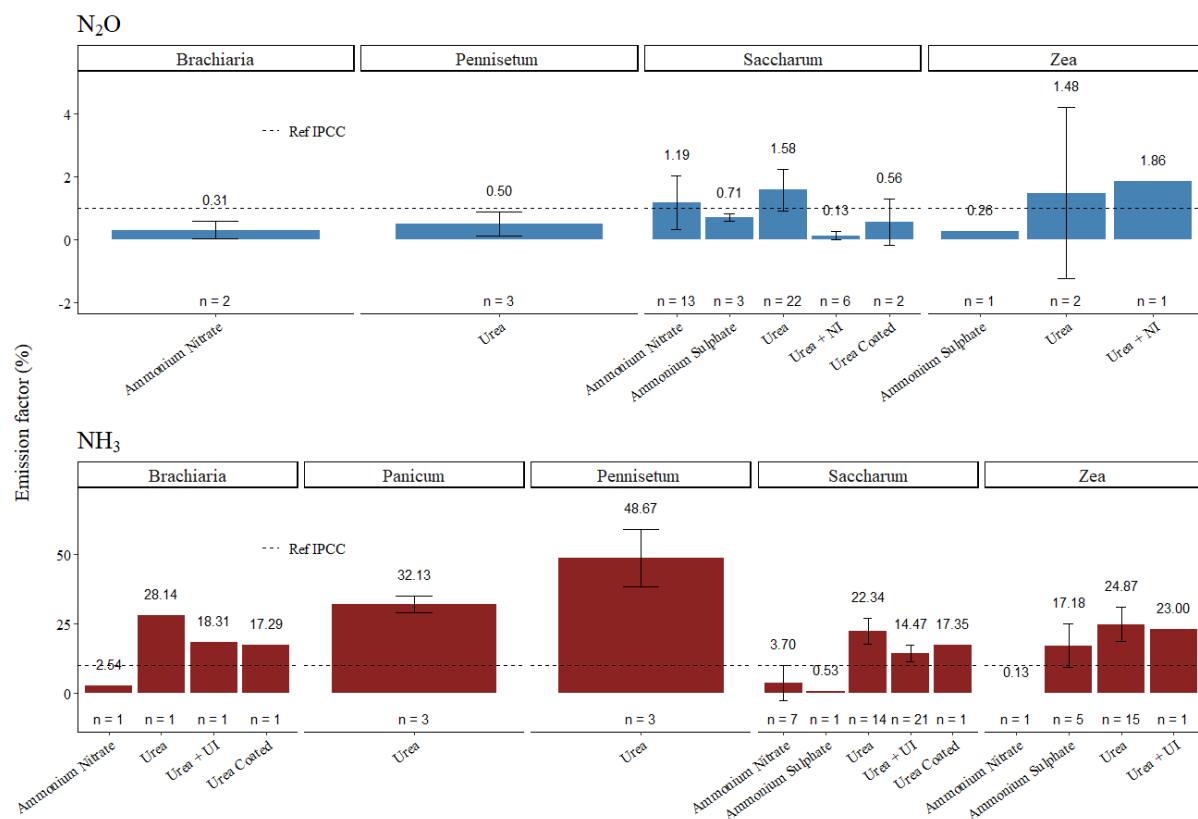


Figure 4. Emission factors for nitrous oxide and ammonia, by fertiliser type and land use. The error bars represent the 95% confidence interval. The dashed horizontal line marks the IPCC default value for N₂O (1%) and NH₃ (11%). Urea+NI: urea applied with nitrification inhibitor; Urea+UI: urea applied with urease inhibitor. The “n” represents the number of experiments.

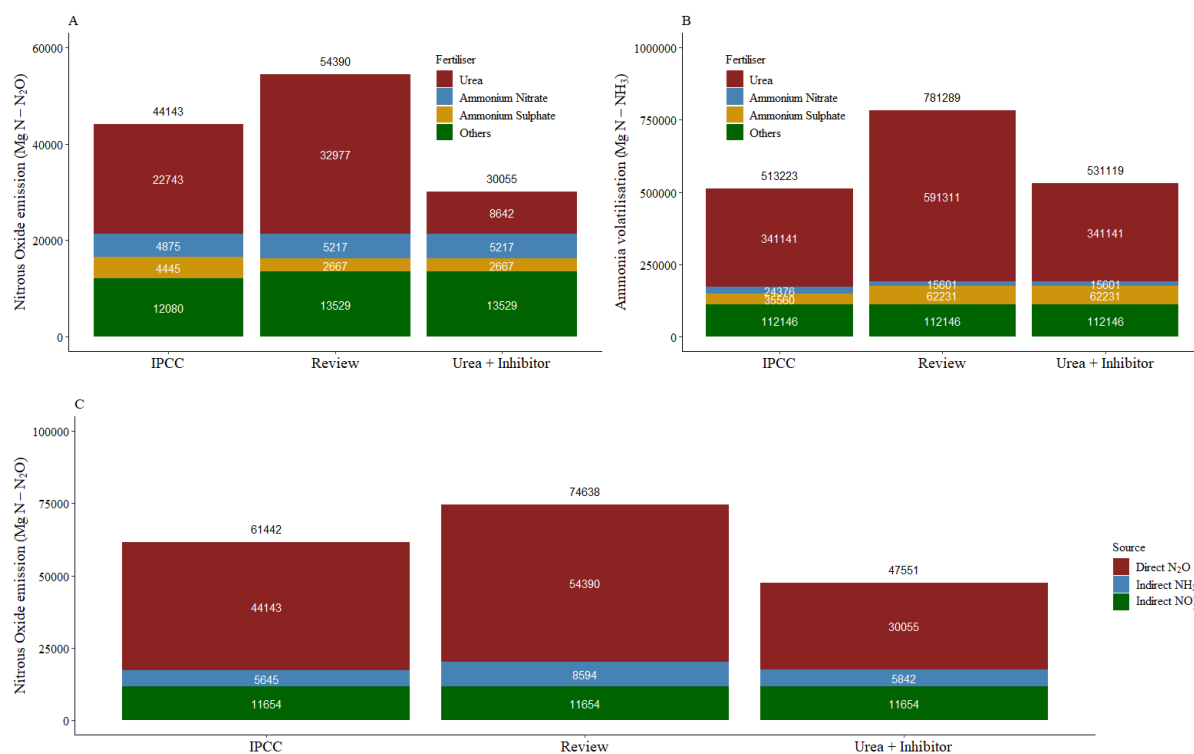


Figure 5 - Final Brazilian N₂O budget for nitrogen fertiliser application in 3 different scenarios: (i) using the Tier 1 IPCC default values (IPCC); (ii) using the reviewed emission factors generated by this study (Review); and (iii) using the reviewed emission factors, considering urea being applied with nitrification and urease inhibitors (Urea + inhibitor). A: Direct nitrous oxide emission (Mg); B: ammonia volatilisation (Mg); C: Total nitrous oxide budget (Mg) summing direct and indirect sources (from NH₃ volatilisation and NO₃⁻ leaching) of N₂O.